

UNCLASSIFIED

AD 4 3 7 2 8 5

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

437285

CATALOGED  
AS AD NO.

437285

APL TDR 64-37

64-12

## AN EXAMINATION OF METHODS FOR CALCULATING VAPOR PRESSURE OF PETROLEUM HYDROCARBON

ALAN E. ZENGEL and HERBERT R. LANDER,  
AF AERO PROPULSION LABORATORY  
WILLIAM G. SCRIBNER, MONSANTO RESEARCH CORPORATION  
JOHN H. WARREN, SOCONY MOBIL OIL COMPANY

TECHNICAL DOCUMENTARY REPORT No. APL-TDR-64-37

MARCH 1964

AF AERO PROPULSION LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 3048, Task No. 304801

## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Defense Documentation Center (DDC), (formerly ASTIA), Cameron Station, Bldg. 5, 5010 Duke Street, Alexandria, Virginia, 22314.

This report has been released to the Office of Technical Services, U.S. Department of Commerce, Washington 25, D. C., in stock quantities for sale to the general public.

Copies of this report should not be returned to the Research and Technology Division, Wright-Patterson Air Force Base, Ohio, unless return is required by security considerations, contractual obligations, or notice on a specific document.

## FOREWORD

This report, part of the in-house research on petroleum hydrocarbon jet fuels by the AF Aero Propulsion Laboratory, was prepared by A. E. Zengel and H. R. Lander of that laboratory with the cooperation of Monsanto Research Corporation and Socony Mobil Oil Company. The contributions to this work by Monsanto Research Corporation were funded by the Technical Support Division, Fuels and Lubricants Branch, under Contract No. AF 33(657)-8193. The cooperation secured from the Socony Mobil Oil Company was funded by that company and contributed at no cost to the government.


The work reported in this document was conducted from April 1963 to July 1963, under Project 3048, Task 304801.

## ABSTRACT

At high temperatures, the vapor pressure of kerosene-type hydrocarbons is difficult to measure accurately with laboratory apparatus. Because of the inherent difficulties in direct measurement of vapor pressure-temperature relationships at high temperatures, the vapor pressure is being determined through calculation techniques. The purposes of this report are to compare the difficulty and accuracy of five techniques, of which three were basic calculation techniques and two were experimental techniques. In an effort to compare the techniques and to determine the precision of a calculation technique, four independent workers calculated the vapor pressure-temperature relationship for one high-quality jet fuel and for one synthetic blend of seven pure hydrocarbons. The results demonstrate that the method of assuming segments of the true boiling point curve to be pure compounds and finding the total vapor pressure as the sum of the component partial pressures is precise to  $\pm 5$  percent. The empirical technique developed by Edmister is less accurate (based on the comparison with experimental results) and less precise than the more laborious true boiling point curve technique. An empirical curve relating the 20-percent point to vapor pressure was found to be within  $\pm 10$  percent of experimental results when applied to fuels with a Reid Vapor Pressure of less than 0.1 psia and a 5 percent to 95 percent ASTM distillation range of less than 200° F.

## PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

  
MARC P. DUNNAM,  
Chief, Technical Support Division  
AF Aero Propulsion Laboratory

## TABLE OF CONTENTS

	PAGE
INTRODUCTION . . . . .	1
CORRELATION METHODS . . . . .	2
General . . . . .	2
British Petroleum Method . . . . .	2
Maxwell Method . . . . .	3
Edmister Method . . . . .	3
20-Percent Method . . . . .	4
EXPERIMENTAL METHODS . . . . .	9
True Boiling Point Apparatus . . . . .	9
Reflux Method . . . . .	9
Isoteniscope Methods . . . . .	10
RESULTS . . . . .	12
REFERENCES . . . . .	15
APPENDIX I Composition of Hydrocarbon Mixture . . . . .	16
APPENDIX II TBP Column Operating Data . . . . .	17
APPENDIX III True Boiling Point Distillation of Hydrocarbon Mixture . . . . .	18
APPENDIX IV True Boiling Point Distillation for RAF-167-60 . . . . .	19
APPENDIX V Inspection Data for RAF-167-60 . . . . .	21

## LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Phase Diagram for RAF-167-60 . . . . .	6
2	0-Percent Vapor Bubble Point Lines for RAF-167-60 . . . . .	7
3	“0-Percent Correlation Method Chart Applicable for Fuels Having an RVP Less Than 0.1 psig and 5 to 95 Percent ASTM Distillation Range Less Than 200°F” . . . . .	8
4	Apparatus for Reflux Method . . . . .	11



## INTRODUCTION

Future supersonic aircraft will operate under temperature conditions that are more severe than those encountered by present subsonic aircraft. The hydrocarbon fuel is the major heat sink during high-speed flight. The fuel will be used to cool the cabin, instruments, and engine oil; in addition, the ram air temperature will be increased with speed so that the fuel in the tanks is exposed to a heat flux from the aircraft skin. The severity of the increased temperature to which the fuel will be subjected has caused concern about the determination of fuel properties which exist at the higher temperatures. Perhaps the most important property to define at the higher temperatures is vapor pressure. Fuel system design, especially fuel tank design, is sensitive to vapor pressure-temperature relationships.

Because of various problems associated with laboratory vapor pressure devices at high temperatures and pressures, correlation techniques are presently considered best for determining the vapor pressure of hydrocarbon fuels. The objectives of our work were to investigate three basic available correlation techniques and techniques for obtaining vapor pressures by experiment, then to compare all techniques for difficulty and accuracy, and finally, to determine the accuracy of correlation techniques by comparing results obtained with the vapor pressures obtained through experimental techniques.

The precision of each technique was evaluated by comparing the results from four independent workers. A satisfactory technique should be one that has a precision of approximately  $\pm 5$  percent and an accuracy of approximately  $\pm 10$  percent.

Checking the accuracy of a vapor pressure correlation technique was not as simple as checking precision. The best method would involve a comparison of the correlation technique with a complete component analysis and theoretical partial pressure calculations that would include corrections for non-ideality. However, the large number of compounds in a typical jet fuel makes this approach impractical. An alternate approach would involve an analysis of the components of the first 5 to 10 percent of the fuel. Since the light ends make the major contribution to the vapor pressure, the accuracy of a vapor pressure determination would be greatly increased if an accurate front end analysis were available. Although this approach is possible through the use of gas-liquid chromatography and mass spectrometry, the cost of such a procedure would be prohibitive, and the time involved would be excessive.

The accuracy of the correlation techniques was based on an accurately blended mixture of pure hydrocarbons.\* A vapor pressure versus temperature relationship was calculated for this mixture since there was accurate knowledge of the composition. The theoretical vapor pressure for the mixture was compared to experimentally-determined vapor pressures and to the correlation-derived vapor pressures to determine the accuracy. The experimental vapor pressures were determined by a glass isoteniscope and by a subatmospheric reflux method.

---

\*See Appendix I for composition of the hydrocarbon mixture.

## CORRELATION METHODS

### GENERAL

Basically, three correlation methods were compared. The first, and most elaborate method, involved dividing the true boiling point curve into segments and assuming that each segment represented a pure compound. The British Petroleum Method and the Maxwell Method are this type of calculation technique. The second basic technique, the Edmister Method, has been developed through empirical correlation. The third technique, the 20-Percent Method, is an empirical method developed for a narrow range of fuels.

### BRITISH PETROLEUM METHOD

The most elaborate calculation method investigated was the one reported by the British Petroleum Company (Reference 1).

Briefly, the method involves the following steps:

1. With the aid of charts developed through empirical correlations, convert the ASTM distillation to a true boiling point plot;
2. Divide the true boiling point curve into twelve or more fractions;
3. Assuming each fraction of the true boiling point curve is a pure compound, calculate the mole fraction using charts relating the normal boiling point of hydrocarbons to specific gravity and molecular weight;
4. With the aid of vapor pressure plots relating the normal boiling points of pure hydrocarbons to vapor pressure at various temperatures, determine the partial pressure due to each fraction at the temperature in question;
5. Total the partial pressures for each fraction to get the true vapor pressure of the fuel at that temperature;
6. Develop a plot of the log of vapor pressure versus the reciprocal of absolute temperature by choosing a number of temperatures.

The accuracy of this method is increased as the number of fractions is increased. However, the practicality of increasing the number of fractions beyond 20 fractions is doubtful because of the questionable validity of assuming an ideal solution and assuming the accuracy of the empirical charts. At first glance, the accuracy of this method would appear to be a function of the care with which the front end of the ASTM distillation was performed. To gain an appreciation for the necessity of an accurate component analysis of the ASTM distillation curve, we performed a true boiling point distillation on RAF-167-60 and the hydrocarbon mixture. A comparison of the results obtained from using an ASTM D-86 distillation curve with the results obtained from starting with the experimental true boiling point distillation demonstrates that the method of calculation is satisfactory with the relatively inaccurate ASTM D-86 distillation and, therefore, is not particularly dependent on the accuracy of the front end distillation determination. For the RAF-167-60 fuel, for example, the average vapor pressure at 150°C (302°F) as determined from the ASTM distillation is 3.55 psia. The average vapor pressure determined from the true boiling point distillation at that temperature is 3.47 psia. Not only is there good agreement between the two approaches to the British Petroleum Method, but the methods are in good agreement with the experimental results from the reflux apparatus and the isoteniscope, both of which gave a vapor pressure of 3.42 psia at 150°C.

## MAXWELL METHOD

An alternate technique for making the same vapor pressure determination may be taken by using the data presented by Maxwell in his "Data Book on Hydrocarbons" (Reference 2). The use of Maxwell's data as presented in the book would require a true boiling point distillation. However, it is possible to start with an ASTM distillation by converting the ASTM distillation plot to a true boiling point plot. This conversion was made by using the empirical charts developed by Edmister (Reference 3). These charts, like those used by British Petroleum, relate the 50 percent evaporated temperatures of the ASTM distillation with the TBP distillation and with the slopes of the distillation curves for various segments of the distillation. Once the true boiling point curve has been developed, the procedure is the same as that used in the British Petroleum Method. The relationship between the normal boiling point of the pseudo-compounds and the API gravity may be found by assuming a constant characterization factor and using Maxwell's chart relating the characterization factor to boiling point and gravity. The additional calculations relating normal boiling point to specific gravity, molecular weight, and vapor pressure are accomplished with the appropriate charts in Maxwell's "Data Book on Hydrocarbons."

A second comparison was made between the results obtained by starting with a true boiling point distillation and by starting with the ASTM distillation for the RAF-167-60 fuel. At 150°C (302°F) the TBP approach gave a vapor pressure of 3.43 psia. The results compare favorably with each other and with the experimental results of 3.42 psia from both the isoteniscope and the reflux apparatus.

## EDMISTER METHOD

The second basic correlation investigated was the empirical correlation technique developed by Edmister (Reference 3). It is possible to develop a complete high pressure PVT phase diagram from an ASTM distillation by using this technique. A complete PVT diagram developed by this method for RAF-167-60 is shown in Figure 1. Edmister, in Reference 3, cautions that vapor pressure lines should not be extrapolated to subatmospheric pressures for heavy oils. This was not a limitation, however, since this work was generally concerned with kerosenes in the high-temperature-high-pressure region. For the purposes of determining the true vapor pressure, it is necessary to develop only the 0 percent vapor bubble point line of the PVT phase diagram.

The 0 percent vapor bubble point line corresponds to the true vapor pressure line which has vapor volume to liquid volume ratio of zero. Previous correlations, published by Edmister and Pollock (Reference 4) in 1948, were found to be less accurate than those published by Edmister and Okamoto (Reference 5) in 1959. The methods published by Edmister in his book (Reference 3) are similar to the Edmister and Pollock correlations but were improved through the use of additional experimental data. A comparison between the two correlations (References 4 and 5) is illustrated on the RAF-167-60 fuel in Figure 2.

Briefly, the steps in the calculation method are accomplished with the aid of Edmister's book, "Applied Hydrocarbon Thermodynamics" (Reference 3), as follows.

1. Convert the ASTM distillation curve to an equilibrium flash vaporization plot. This conversion is made by using the empirical correlations between the ASTM 50 percent point and the EFV 50 percent point, and the ASTM and EFV slopes for various segments of the distillation curve.

2. Determine the critical temperature from the chart relating the volumetric average boiling point and API gravity to the difference between the critical temperature and the volumetric average boiling point.
3. Determine the critical pressure from the chart relating ASTM volumetric average boiling point, API gravity, and 10 percent to 90 percent ASTM slope to the critical pressure.
4. With a knowledge of the critical temperature, determine the focal point temperature from the chart relating ASTM volumetric average boiling point and the 10 percent to 90 percent ASTM slope to the difference between the focal temperature and the critical temperature.
5. With a knowledge of the critical pressure, determine the focal point pressure from the chart relating ASTM volumetric average boiling point and the 10 percent to 90 percent ASTM slope to the difference between focal pressure and critical pressure.
6. Plot the 0 percent vaporized line of the PVT diagram by drawing a straight line, from the focal point to the EFV initial boiling point at 14.7 psia, on a plot relating the log of the vapor pressure to the reciprocal of absolute temperature.

In general, the Edmister technique is not as accurate as the true-boiling-point-fraction technique. The results were low for both the RAF-167-60 fuel and the hydrocarbon mixture. At 200°C for example, the RAF-167-60 fuel had an average vapor pressure of 12.4 psia. The true-boiling-point-fraction method, by contrast, yielded a vapor pressure of 14.06 psia starting with the ASTM curve, and 13.70 psia starting with the data for the true boiling point. The isoteniscope and the reflux determination gave values of 13.19 psia and 13.34 psia, respectively.

## 20-PERCENT METHOD

The third correlation method investigated was based on Maxwell's data which relates the 20 percent evaporated temperature to the true vapor pressure (Reference 6). The correlation chart used in this study has been reproduced in Figure 3, and has been adapted from Maxwell's 1955 vapor pressure-temperature correlations. Maxwell's work concerned vapor pressure-temperature correlations for pure hydrocarbons and very narrow boiling fractions (Reference 7). Though the Maxwell work is for pure compounds and narrow fractions, the charts can be utilized for fuels, providing they have a Reid vapor pressure of less than 0.1 psia and a 5 to 95 percent ASTM distillation range of less than 200°F.

In applying the correlation in Figure 3, it was noticed that the agreement between the true-boiling-point-fraction technique and the experimental measurements with the vapor pressure picked off the chart was improved when a stem correction for the 7F thermometer used in the ASTM D-86 distillation was applied. The 7F thermometer specified for the ASTM D-86 distillation is a total immersion thermometer. If a temperature is required, rather than a thermometer reading, correction must be made for the portion of the thermometer that is exposed to the ambient temperature. For the RAF-167-60 fuel, the average vapor pressure at 200°C or 392°F is 14.06 psia by the British Petroleum Method and 13.19 psia by the isoteniscope. The 20 percent correlation without the stem correction is 14.80 psia and with the stem correction is 13.80 psia. The effect of the stem correction is illustrated in Table 1 for RAF-167-60.

TABLE 1  
RAF-167-60 VAPOR PRESSURE AT 300°F

Method	Pressure (psia)
Reflux	3.29
Isoteniscope	3.29
TBP - BP calculation	3.38
ASTM - BP calculation	3.56
ASTM - 20% point (no stem correction)	4.0
ASTM - 20% point (stem correction applied)	3.5

At the time of this writing, we did not know whether or not a stem correction had been applied originally to the ASTM data used to develop the 20 percent correlation shown in Figure 3. However, since the ASTM D-86 procedure does not specify a stem correction, it was believed that the 20 percent correlation was developed from raw ASTM distillation data without the stem correction.

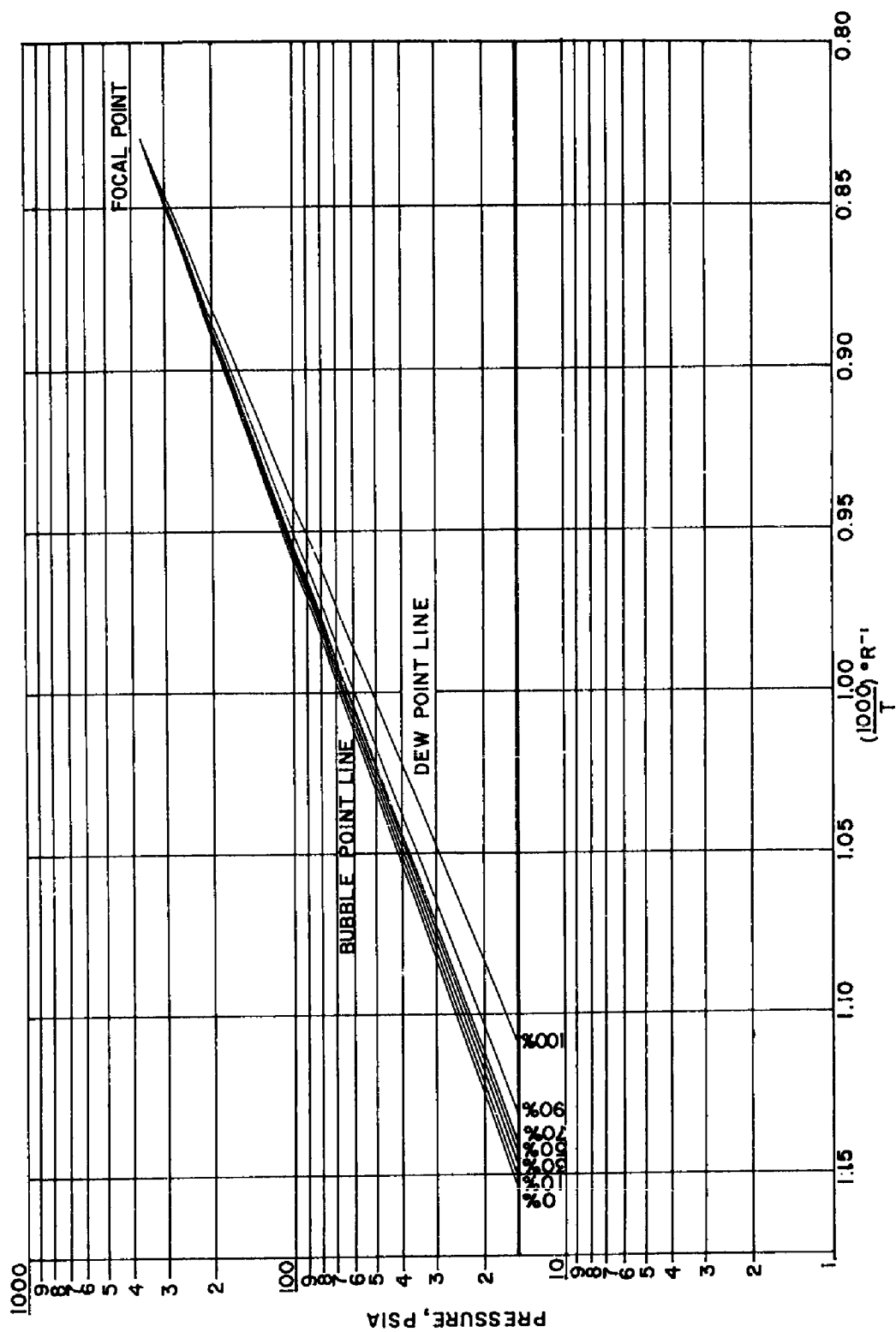


Figure 1. Phase Diagram for RAF-167-60

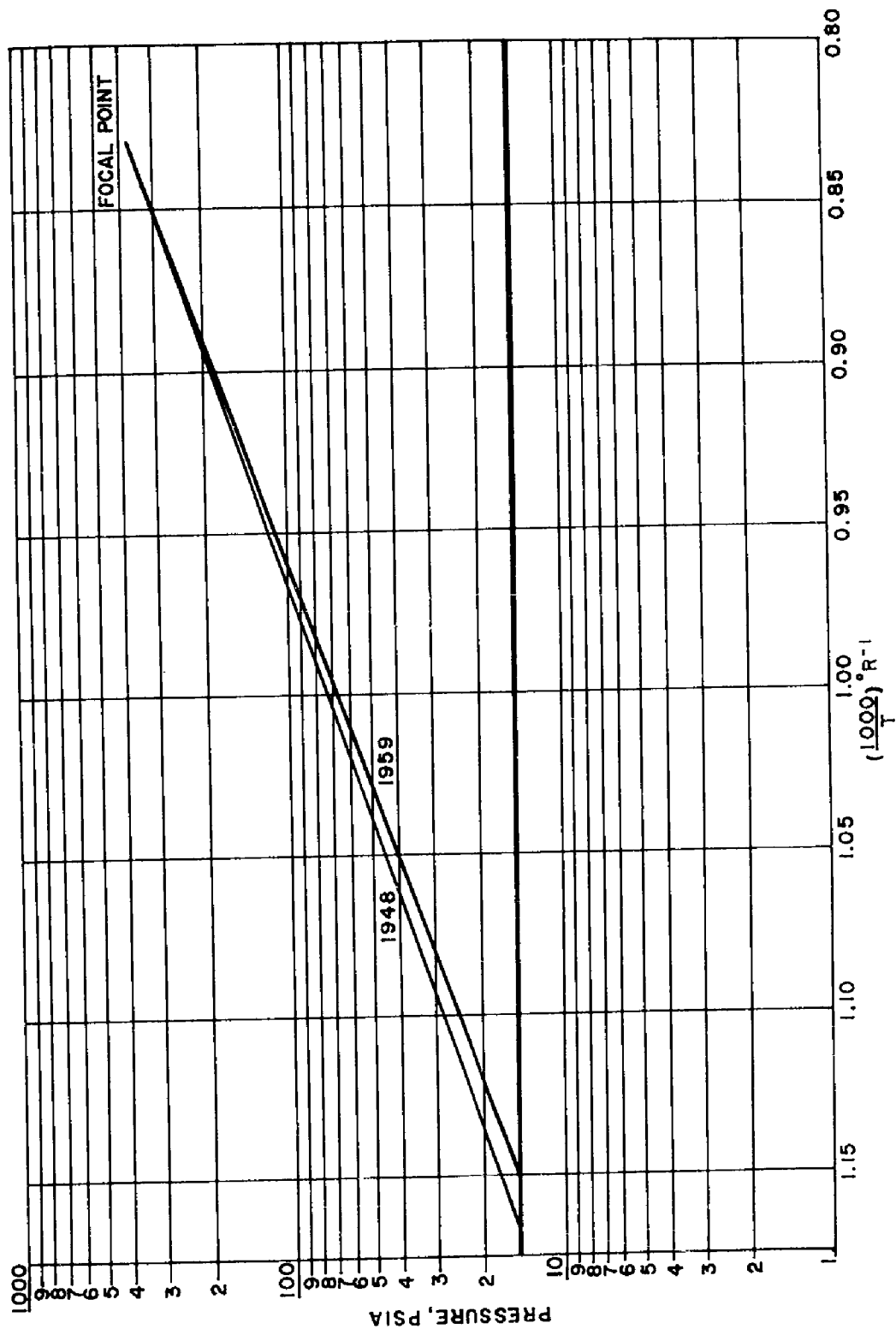


Figure 2. 0-Percent Vapor Bubble Point Lines for RAF-167-60

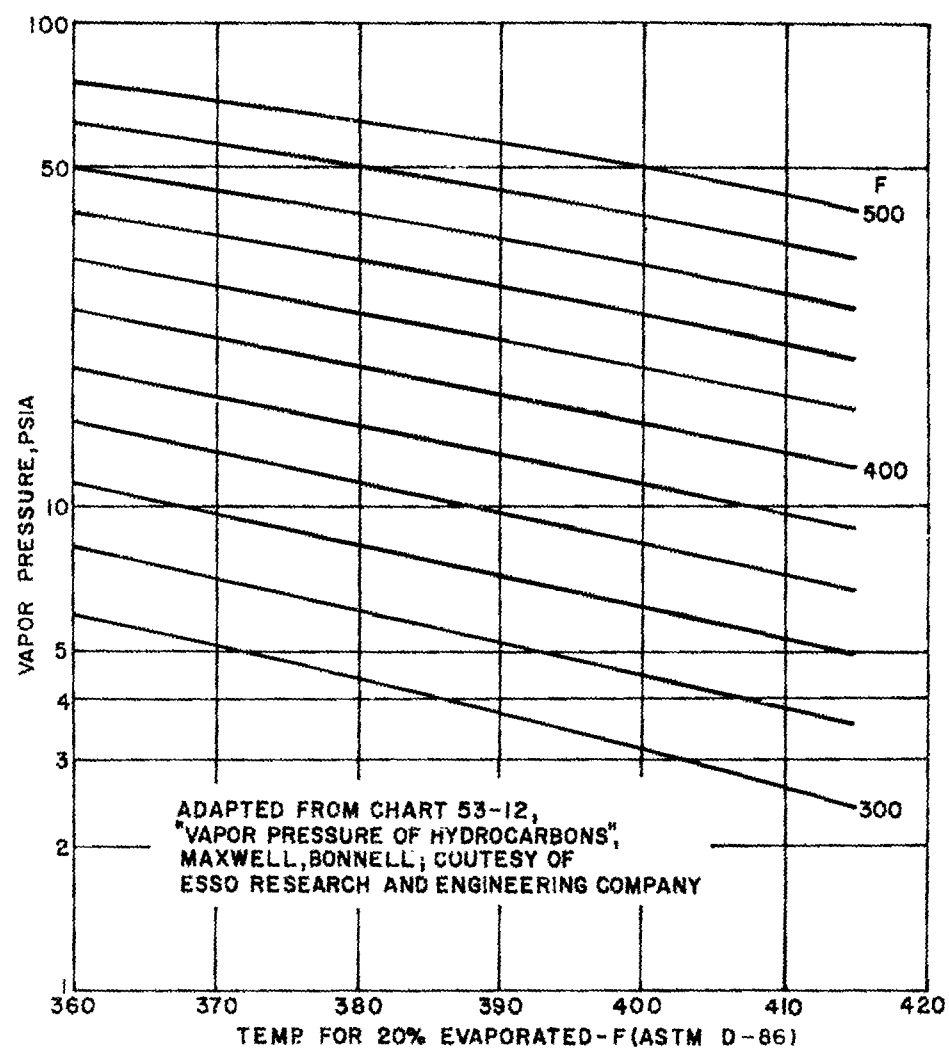


Figure 3. "0-Percent Correlation Method Chart Applicable for Fuels Having an RVP Less Than 0.1 psig and 5 to 95 Percent ASTM Distillation Range Less than 200° F"



## EXPERIMENTAL METHODS

### TRUE BOILING POINT APPARATUS

W. L. Nelson, in his "Petroleum Refinery Engineering" (Reference 8), describes True Boiling Point (TBP) distillation apparatus as "Any equipment that accomplishes a good degree of fractionation . . . ." It is of interest to note that TBP is a loose term generally applicable to any apparatus that achieves better separation than the simple ASTM distillation. In any case, no specific apparatus is designated exclusively for this use; thus, the equipment and variations of the same equipment utilized throughout the petroleum industry are as numerous as the companies involved. Two different types of TBP apparatus, the Podbielniak High Temperature Distillation Apparatus and the Nester Spinning Band Distillation Column, were used in the analyses for this report.

#### Podbielniak High Temperature Distillation Apparatus

The unit used to effect separation of the components of the hydrocarbon mixture was a highly efficient packed column manufactured by Podbielniak Inc. The column utilizes a Heli-Grid integral packing which is generally considered to have the highest efficiency of all laboratory column packings in terms of the efficiency factor (boil-up rate x number of plates/column hold-up). The column has a capability of 30 to 115 theoretical plates, depending on throughput. Operating characteristics for this unit are given in Appendix II. The true boiling point data are presented in Appendix III.

#### Nester Spinning Band Distillation Column

The Nester Spinning Band Column, used in the TBP distillation of RAF-167-60, is designed for fractionation of high-boiling heat-sensitive liquids. It can be operated at extremely low pressures (down to  $10^{-5}$  mm Hg) and thus have very small operating hold-up.

The unit used in this operation employs a stainless steel gauze-type spinning band that is slightly less in diameter than the inner diameter of the column. During operation, the band spins in excess of 1000 rpm, thus violently agitating the reflux liquid and producing large vapor diffusion coefficients. The violent contact of liquid reflux and ascending vapors provides good fractionation. The main disadvantage to the unit is that the low number of theoretical plates (approximately 25 for this operation) limits the sharp component separations possible in the more efficient packed columns. Nevertheless, in distillations for TBP curves of petroleum fractions containing many components boiling within 2, 1, or even  $1/2^{\circ}\text{F}$  of each other, use of higher efficiency columns would not materially alter the results. The true boiling point data for RAF-167-60 are presented in Appendix IV.

### REFLUX METHOD

The Reflux method, one of the experimental methods used, is described in Reference 9 as follows:

"An equilibrium condition of vapor evolution and refluxing of the evolved vapors is made under conditions of fixed vacuum (pressures below atmosphere) by applying heat to the test fluid. Equilibrium conditions exist when the temperature of the fluid and the temperature of the refluxing vapors

approach each other and maintain a constant minimum temperature differential. The system pressure at which equilibrium refluxing occurs is regarded as the vapor pressure of the test fluid for the particular liquid temperature observed. Similar 'boiling points' are obtained by gradually increasing the system pressure step-wise up to atmospheric pressure. By plotting liquid temperature against system pressure, a smooth curve is obtained from which vapor pressure below atmospheric pressure may be obtained at any desired temperature."

The apparatus employed (Figure 4) was essentially that described in the above reference quotation. Modifications included the introduction of an additional dry-ice trap and a "shock-coil" to minimize the possibility of breakage.

### ISOTENISCOPE METHODS

Two variations of the Isoteniscope method, the second of the experimental methods used, were tried during the investigation. The variations were the use of a glass isoteniscope and the use of a high-pressure-high-temperature isoteniscope

#### Glass Isoteniscope

Vapor pressures of RAF-167-60 were measured in a horizontal-chamber glass isoteniscope (Reference 13) with a vapor to liquid volume ratio of 1. In this apparatus, the material to be tested is used to form a differential manometer in a U-tube for the detection of equilibrium between vapor pressure of the material in the sample and the external measurable pressure.

The apparatus and the experimental procedure are fully described in Reference 13.

#### High-Pressure-High-Temperature Isoteniscope

The high-pressure-high-temperature isoteniscope is described and illustrated by Johns, McElhill and Smith in Reference 11. It consists of a steel or monel reaction vessel, or bomb, 2 1/2 inches in diameter by 5 inches in length, having a base part and a detachable head. One to five grams of sample are introduced into a 10- to 15-ml. cup in the bottom of the bomb. The sample cup is covered by a thin metal diaphragm on which the head is placed. The head seals the diaphragm to a lip at the top of the sample cup when it is secured by cap screws. A small insulated metal rod passes through the head to touch the diaphragm, completing an electrical circuit that activates a solenoid pressure valve that feeds nitrogen to the top of the diaphragm through the head. A thermocouple inserted into a well in the bottom of the bomb measures the bomb temperature.

As the sample is heated, its increased pressure pushes the diaphragm up against the contact rod which then activates the solenoid valve to admit enough nitrogen to balance the pressure of the sample. The pressure of the nitrogen is measured by either a low-pressure (300 psia) or a high-pressure (2000 psia) Heise gage. Thus, a series of pressure-temperature points may be obtained as the bomb is heated. The pressure may range from a few pounds per square inch to 1500 psia, while the temperature may vary from ambient to 1000°F.

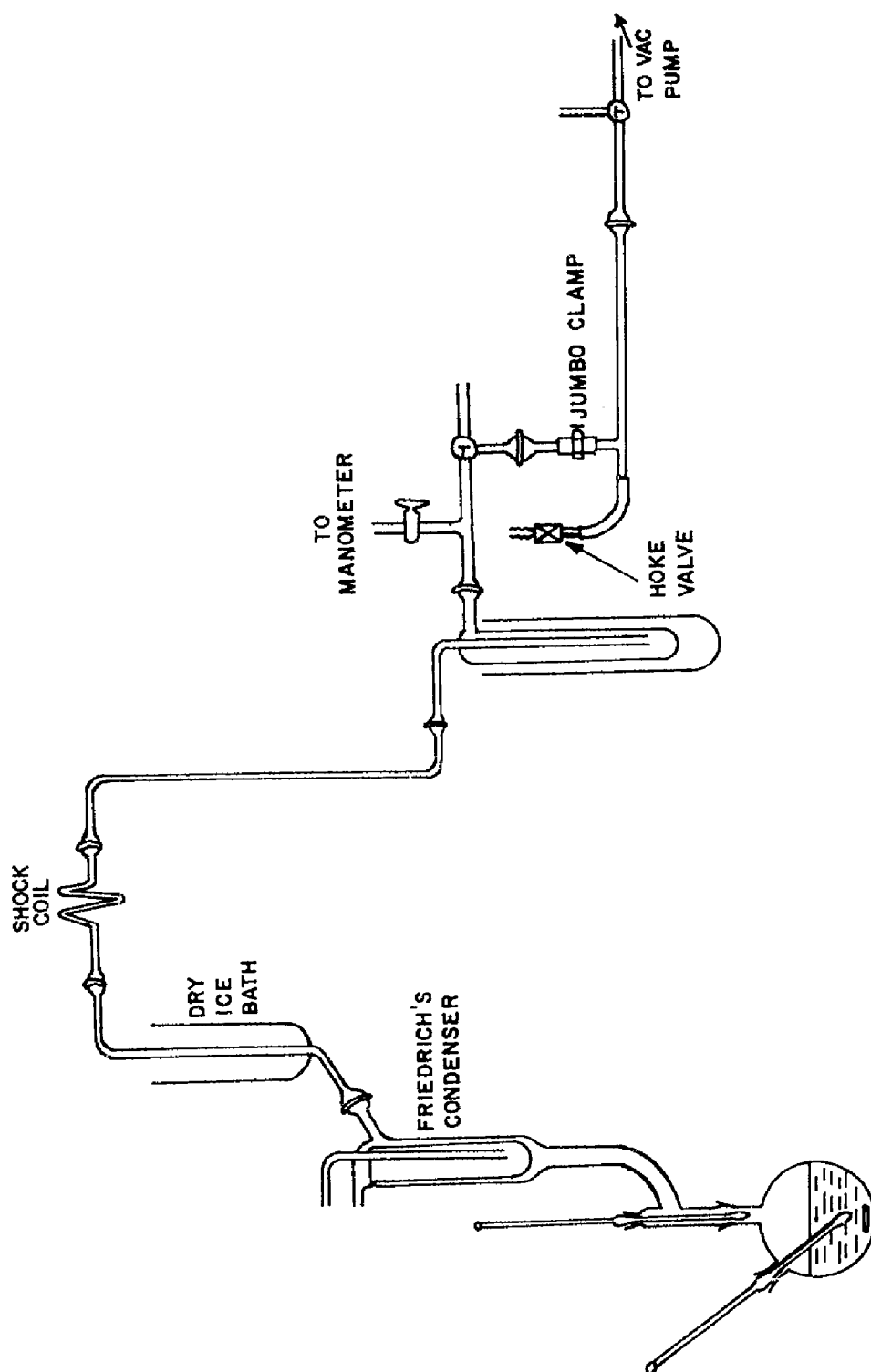


Figure 4. Apparatus for Reflux Method

## RESULTS

The RAF-167-60 fuel was extensively studied by using various calculation and experimental techniques. The inspection data for this fuel appears in Appendix V. Rough gas chromatographic and mass spectrometric analyses on this fuel showed that the main constituent was dodecane.

The results of the calculated and experimental vapor pressure methods are presented in Table 2.

TABLE 2  
VAPOR PRESSURE RAF-167-60 (psia)

Temperature	75°C	100°C	150°C	200°C	250°C
Results					
Experimental					
Glass Isoteniscope	- - -	- - -	3.42	13.19	39.45 <sup>d</sup>
Reflux Method	- - -	0.53 <sup>d</sup>	3.42	13.34	- - -
Calculated					
TBP-Fraction	0.158	0.56	3.65	14.4	41.7 (12) <sup>a</sup>
(ASTM) <sup>b</sup>	0.160	0.53	3.50	13.6	40.2 (16)
	0.160	0.56	3.44	13.9	40.6 (19)
	0.160	0.51	3.61	14.4	42.1 (16)
TBP-Fraction	0.156	0.52	3.48	13.7	39.7 (18)
(experimental	0.160	0.53	3.60	13.9	41.1 (19)
curve) <sup>c</sup>	0.150	0.51	3.40	13.5	40.1 (14)
	0.140	0.52	3.41	13.7	40.4 (15)
Edmister	- - -	- - -	- - -	12.3	37.0
	- - -	- - -	2.70 <sup>d</sup>	12.3	34.0
	- - -	- - -	4.40 <sup>d</sup>	12.7	38.0
Maxwell-Fraction					
ASTM curve	0.154	0.52	3.43	14.6	41.8 (15)
TBP curve	0.144	0.50	3.25	15.2	39.6 (14)
(experimental)					
a - numbers in parenthesis are number of fractions					
b - method used starting with ASTM D-86 distillation					
c - method used starting with experimental TBP data					
d - extrapolated					

It should be noted that the results obtained from the Edmister correlations are lower than the results from the experimental methods and the results from the British Petroleum calculations. Also, the results of the British Petroleum calculations are essentially the same starting with either an ASTM D-86 distillation or a true boiling point distillation. This is encouraging because it demonstrates that this method may be used with confidence with the inexpensive ASTM distillation.

In a further attempt to investigate the accuracy of the correlation methods, a mixture of hydrocarbons (composition given in Appendix I) was accurately compounded and tested experimentally. The results of the correlation and experimental techniques are shown in Table 3. The vapor pressures for the pure compounds used in the hydrocarbon mixture were determined with the aid of API project data (Reference 12) and Jordon's data (Reference 10). It is readily apparent that the vapor pressures predicted from a knowledge of the composition are consistently lower than those predicted by the correlation methods. The investigators feel that this discrepancy is due to the non-ideality of the hydrocarbon mixture.

The variations in the theoretical calculation for vapor pressures for the hydrocarbon mixture demonstrate the precision to be expected among independent workers. The variations in the theoretical calculations are due to such considerations as rounding errors in the calculations. The true-boiling-point-fraction method also has errors introduced through the empirical charts and should be less precise than the calculations made from a knowledge of the hydrocarbon mixture composition.

TABLE 3  
VAPOR PRESSURE HYDROCARBON MIXTURE (psia)

Temperature	75° C	100° C	150° C	200° C	250° C
Results					
Experimental Reflux Method	2.19	4.76	16.8	- - -	- - -
Hi-temperature Isoteniscope	2.7	5.4	17.5	46.0	100
Calculation					
Compositional analysis	2.33 2.30 2.29 2.29	5.20 5.10 5.12 5.20	19.4 19.3 18.9 18.7	55.1 54.2 54.6 53.2	128 - - - - - - 124
TBP-Fraction (ASTM) <sup>c</sup>	2.14 2.30 2.43	4.96 5.10 5.26	18.6 17.8 19.8	51.8 50.4 53.6	118 (14) <sup>a</sup> 120 (12) - - (17)
TBP-Fraction (experimental curve) <sup>d</sup>	2.04 2.30 2.16 <sup>b</sup> 1.96 2.08 2.04	4.77 5.18 5.04 4.35 4.76 4.62	17.7 18.3 18.5 - - - 17.9 17.0	51.1 50.6 53.3 51.0 50.4 - - -	- - ( 8) 119 (18) - - ( 8) - - (18) - - (18) 116

TABLE 3 (Continued)

Temperature	75°C	100°C	150°C	200°C	250°C
Edmister	- - -	- - -	18.0	46.0	100
	- - -	5.8	18.2	46.0	97
	- - -	- - -	18.0	46.0	100
a - numbers in parentheses are number of fractions b - true molecular weights used c - method used starting with ASTM D-86 distillation d - method used starting with experimental TBP data					

The 20-percent correlation results are given in Table 4. These results have been compared to those obtained with the true-boiling-point-fraction method to demonstrate the effect of thermometer-stem corrections. In Table 4, data on JP-6 and RAF-157-60 fuels are included for comparison with RAF-167-60.

TABLE 4

## RESULTS FROM 20-PERCENT METHOD

Fuel	Temperature (°F)	British Petroleum Method	20-Percent (Corrected)	20-Percent (Uncorrected)
RAF-167-50	302	3.44	3.42	3.60
	392	13.9	13.8	14.8
RAF-157-60	302	1.83	1.75 <sup>a</sup>	1.93 <sup>a</sup>
	392	8.28	7.80 <sup>a</sup>	8.80 <sup>a</sup>
JP-6	302	11.1	10.9 <sup>a</sup>	12.1 <sup>a</sup>
	392	36.0	36.2 <sup>a</sup>	40.0 <sup>a</sup>
Note: a indicates extrapolated values				

## REFERENCES

1. The Calculation of the Vapour Pressures of Aviation Fuels. The British Petroleum Company Limited, BP Research Centre, Petroleum Division, Sunbury-On-Thames, Technical Memorandum No. 110.040, 20 June 1960.
2. Maxwell, J. B. Data Book on Hydrocarbons. 1st ed., Van Nostrand, New Jersey. First Edition. 1950.
3. Edmister, Wayne C. Applied Hydrocarbon Thermodynamics. Gulf Publishing Company. Volume 1. 1961.
4. Edmister, Wayne C. and Pollack, D. H. "Phase Relations for Petroleum Fractions." Chemical Engineering Progress. Vol. 44, No. 12, p. 905. December 1948.
5. Edmister, Wayne C. and Okamoto, K. Keith. "Applied Hydrocarbon Thermodynamics." Petroleum Refiner. August 1959.
6. Chart FL60-17. Pratt & Whitney Aircraft. January 27, 1960.
7. Maxwell, J. B. and Bonnell, L. S. Vapor Pressure Charts for Petroleum Hydrocarbons. Esso Research and Engineering Company, Linden, N. J. April 1955.
8. Nelson, W. L. Petroleum Refinery Engineering. Edition IV McGraw-Hill, New York. Edition IV. 1958.
9. Reflux Method for Determination of Vapor Pressures of Liquids Below Atmospheric Pressure. FL-60-18. Pratt & Whitney Aircraft. January 18, 1961.
10. Jordon, Earl T. "Vapour Pressure of Organic Compounds." Interscience. New York. 1954.
11. Johns, I. B., McElhill, E. A., Smith, J. O. Ind. Eng. Chem., Prod. Res. Devel. 1, 2. 1962.
12. American Petroleum Institute. Research Project 42. Pennsylvania State University, University Park, Pa.
13. Blake, E. S., et al., Chem. and Eng. Data, 6, 87. 1961.

## APPENDIX I

### COMPOSITION OF HYDROCARBON MIXTURE

<u>Components of Hydrocarbon Mixture</u>	<u>Volume in Mixture (Percent)</u>	<u>Minimum Component Purity (Percent)</u>
n-Heptane	3.0	99+
Isooctane	3.0	99+
Benzene	3.0	99+
Toluene	10.0	99+
n-Decane	35.0	99.5
n-Dodecane	30.0	99.5
n-Cetane	16.0	99.5



# APPENDIX II

## TBP COLUMN OPERATING DATA

ITEMS AND CONDITIONS	FUEL					
	Hydrocarbon Mixture			RAF-167-60		
<u>Column Type</u>	Podbielniak "Hyper-Cal"			Nester Spinning Band		
<u>Packed Section</u>						
Packing	Heli-Grid			Spin Band		
Diameter, mm	8			10		
Height, Inches	36			24		
<u>Theoretical Plates at Total Reflux</u>	55			25		
<u>Distillation Conditions</u>						
Charge Volume, ml.	500			200		
Boil-up Rate, ml./hr	200			300		
<u>Takeoff Rate, ml./hr</u>	<u>Pressure</u> (mm Hg)	<u>Cumula-</u> <u>tive % of</u> <u>Charge</u>	<u>Rate</u> (ml./h)	<u>Pressure</u> (mm Hg)	<u>Cumula-</u> <u>tive % of</u> <u>Charge</u>	<u>Rate</u> (ml./h)
	760	0-20	15	760	0-50	30
	760	20-55	40	10	50-97	50
	20	55-84	40			
	5	84-95	30			

## APPENDIX III

TRUE BOILING POINT DISTILLATION  
OF HYDROCARBON MIXTURE

<u>Temp. °F</u>	<u>Vol. ml.</u>	<u>Cumulative Volume (ml.)</u>	<u>Vol. %</u>	<u>Cumulative Volume %</u>
175	7.0	7	1.4	
175	3.0	10	0.6	2.0
180	5.0	15	1.0	3.0
195	5.0	20	1.0	4.0
200	5.0	25	1.0	5.0
205	10.0	35	2.0	7.0
215	5.0	40	1.0	8.0
220	5.0	45	1.0	9.0
225	15.0	60	3.0	12.0
227	25.0	85	5.0	17.0
227	8.0	93	1.6	18.6
227	2.0	95	0.4	19.0
240	1.0	96	0.2	19.2
330	1.0	97	0.2	19.4
336	3.0	100	0.6	20.0
340	5.0	105	1.0	21.0
340	20.0	125	4.0	25.0
340	25.0	150	5.0	30.0
340	50.0	200	9.9	39.9
340	75.0	275	14.9	54.8
385	2.0	277	0.4	55.2
420	1.0	278	0.2	55.4
421	39.0	317	7.8	63.2
421	30.0	347	6.0	69.2
421	30.0	377	6.0	75.2
421	10.0	387	2.0	77.2
421	10.0	397	2.0	79.2
421	10.0	407	2.0	81.2
421	15.0	422	3.0	84.2
558	15.0	437	3.0	87.2
558	10.0	447	2.0	89.2
564	20.0	467	4.0	93.2
564	8.0	475	1.6	94.8
Bottoms	26.1	501		100.0

# APPENDIX IV

## TRUE BOILING POINT DISTILLATION FOR RAF-167-60

	<u>Temp.</u> <u>(°F)</u>	<u>Material Balance</u>		<u>Yield</u>	
		<u>Vol. ml.</u> <u>At 60°F</u>	<u>Wt. (gram)</u>	<u>Vol. (%)</u>	<u>Wt. (%)</u>
Sample Size		198.8	154.50		
Overhead	472	193.5	149.92	97.3	97.0
Bottoms	472+	5.3	4.58	2.7	3.0
Total		198.8	154.50	100.0	100.0

<u>Temp. (°F)</u>	<u>Cut (ml.)</u>	<u>Cumulative</u> <u>Cut (ml.)</u>	<u>Cut Vol. (%)</u>	<u>Cumulative Cut,</u> <u>Vol. (%)</u>
332	2.0		1.0	
360	"	4.0	"	2.0
370	"	6.0	"	3.0
373	"	8.0	"	4.0
378	"	10.0	"	5.0
380	"	12.0	"	6.0
381	"	14.0	"	7.0
381-1/2	"	16.0	"	8.0
383	"	18.0	"	9.0
384	"	20.0	"	10.0
384-1/2	4.0	24.0	2.0	12.0
386	"	28.0	"	14.0
386-1/2	"	32.0	"	16.0
387	"	36.0	"	18.0
388	"	40.0	"	20.0
389	"	44.0	"	22.0
389-1/2	"	48.0	"	24.0
390	"	52.0	"	26.0
391	"	56.0	"	28.0
391	"	60.0	"	30.0
391-1/2	5.0	65.0	2.5	32.5
393	"	70.0	"	35.0
393-1/2	"	75.0	"	37.5
395	"	80.0	"	40.0
395-1/2	"	85.0	"	42.5
397	"	90.0	"	45.0
398	"	95.0	"	47.5
1 atm 399	"	100.0	"	50.0

# APPENDIX IV (Continued)

	<u>Temp. (°F)</u>	<u>Cut (ml.)</u>	<u>Cumulative Cut (ml.)</u>	<u>Cut, Vol. (%)</u>	<u>Cumulative Cut, Vol. (%)</u>
Dist. at 10 mm Vac.					
389		5.0	105.0	2.5	52.5
391		"	110.0	"	55.0
392		"	115.0	"	57.5
394		"	120.0	"	60.0
396		"	125.0	"	62.5
399		"	130.0	"	65.0
401-1/2		"	135.0	"	67.5
405		"	140.0	"	70.0
408-1/2		"	145.0	"	72.5
412		"	150.0	"	75.0
415		"	155.0	"	77.5
420		"	160.0	"	80.0
424-1/2		"	165.0	"	82.5
430		"	170.0	"	85.0
438		"	175.0	"	87.5
445		"	180.0	"	90.0
454-1/2		"	185.0	"	92.5
464		"	190.0	"	95.0
472		"	195.0	"	97.5
Bottoms		5.0	200.0	2.5	100.0

# APPENDIX V

## INSPECTION DATA FOR RAF-167-60

Gravity, API	50.6
% w, Hydrogen	15.0
Heat Comb, Btu/lb Net	18850
Luminometer Number	84
Smoke Point, mm	33
Arom, % v FIA	4
Naph, % v UV	0.15
Bromine No.	18.5
ACP, °F	175
Freeze Point, °F	B-72
Flash Point, TCC, °F	150
Visc, cs at 100°F	1.52
at 0°F	5.20
at -30°F	10.23
ASTM Dist, °F	
I.B.P.	378
5	387
10	388
20	390
30	392
40	394
50	396
60	400
70	404
80	410
90	425
95	444
E.P.	477
Recovered, %	98.5
Residue, %	1.0
Loss, %	0.5
Color, Saybolt	18
Water Tolerance	2
Water Reaction	2
Exist Gum, mg/100 ml.	1
Pot Gum, 16 hr	1
100°C, mg/100 ml.	
Mercaptan S, % w	Nil
Sulfur, % w	0.004
Copper Corr, 212°F	1B
Copper, mg/liter	Nil
MFS, mg/gal. Avg.	3.4
Range	3.0-4.2

**UNCLASSIFIED**

**UNCLASSIFIED**